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Nitric Oxide Reduction of the Copper(II) Complex $Cu(dmp)_2^{2+}$ (dmp = 2,9-Dimethyl-1,10-phenanthroline)

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Nitric oxide (NO) has important roles in both environmental[1] and biological chemistry,[2] and the recent discoveries of a variety of bioregulatory and immune response roles for NO in the latter area have made it the subject of intensive experimental research. The bioregulatory functions of NO are generally attributed to interactions between NO and Fe(II/III) centers of certain heme proteins, but reactions with other metal centers are of concern.[3] NO has been demonstrated to be a reductant in reactions with Co(II) and Fe(II) halides as well as Fe(III) porphyrins and ferrihemoproteins.[4] Given the importance of Cu(I/II) couples in biological redox systems,[5] the Cu−NO interaction may also be of interest; indeed the NO reactions of different types of copper proteins have been qualitatively described.[6] In this context, the redox reactions between NO and certain Cu(II) complexes are being examined in this laboratory. Described here is a preliminary report of the nitric oxide reduction of $Cu(dmp)_2^{2+}$ (**I,** dmp = 2,9-dimethyl-1,10-phenanthroline) in solution, which we believe to be the first quantitative demonstration of NO reduction of a cupric complex. Of further interest, reaction with **I** may have potential as a chemical NO sensor.

The reduction potential for $Cu(dmp)_2^{2+}$ (0.58 V vs NHE in water)[7] is substantially more positive than that for most other cupric complexes. This apparently reflects steric effects of the 2,9-dimethyl substituents of the dmp ligand, which force **I** out of a planar geometry, making it a stronger oxidant than the 1,10-phenanthroline analog $Cu(phen)_2^{2+}$ (0.08 V).[7] A similar coordination geometry argument has been invoked to rationalize the positive redox potentials of "blue" copper proteins.[8]

In deaerated solutions of neat H_2O, neat CH_3OH, or methanol/dichloromethane mixtures, $Cu(dmp)_2^{2+}$ was very rapidly reduced to $Cu(dmp)_2^{+}$ (**II**) upon addition of excess NO. The formation of the cuprous complex was clearly observed by the characteristic metal to ligand charge transfer band centered at 454 nm in the optical absorption spectrum. The reaction was determined to be quantitative from the spectral changes as calculated from the known extinction coefficients.[9] **II** was recovered as its triflate (OTf = $CF_3SO_3^-$) salt from the reaction of **I** plus NO in methanol, and its identity was confirmed by ^1H NMR.[10] Dichloromethane solutions of this salt displayed the characteristic emission spectrum of **II** ($\lambda_{max} \sim 680$ nm).[11] Notably, when the reaction was carried out in CH_2Cl_2 solution with low concentrations of MeOH (<1%) under $P_{NO} = 1$ atm, the reaction solutions themselves were observed to be emissive, with the emission intensity increasing with time as the reduction proceeded.

Analysis of the methanol reaction solution by GC-MS demonstrated the presence of methyl nitrite (CH_3ONO; *m/z* 44, 46, 60, 61). Furthermore, GC analysis of the products from the reaction in mixed CH_2Cl_2/CH_3OH solution quantitatively showed that the mole ratio of $CH_3ONO/Cu(dmp)_2^{+}$ formed was unity. When the reaction was instead carried out in an unbuffered aqueous solution, the solution pH was observed to decrease from pH 6 to pH 3 in a manner consistent with acid formation according to eq 1. Nitrite, NO_2^-, was also detected

$$Cu(dmp)_2^{2+} + ROH + NO \rightarrow Cu(dmp)_2^{+} + RONO + H^+ \quad (1)$$

as a product of the reaction in aqueous solutions by the Griess analytical method.[12] Thus the overall reaction is as shown in (1).

No reaction was observed in neat CH_2Cl_2 or neat CH_3CN solution, indicating the importance of the hydroxylic solvent in providing a reagent that can react with the coordinated NO (*vide infra*). Similar trends were observed qualitatively by Olson and Wayland[4b] for the reductive nitrosylation of the ferric tetraphenylporphyrin complex Fe(TPP)Cl.

Preliminary rate measurements carried out spectrophotometrically in mixed CH_2Cl_2/MeOH solutions indicate the reaction kinetics to be dependent on the concentration of methanol. At low methanol concentrations, there is a linear relationship

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(10) (a) The ^1H NMR spectrum of the $Cu(dmp)_2^{+}$ product isolated from the reaction of $Cu(dmp)_2^{2+}$ with NO in CD_3OH gave a spectrum identical to that for an independently prepared $Cu(dmp)_2PF_6$ sample: δ 8.65, 8.61 (2H, d); δ 8.13 (2H, s); δ 7.90, 7.85 (2H, d); δ 2.45 (6H, s). The free ligand dmp gave δ 8.31, 8.27 (2H, d); δ 7.82 (2H, s); δ 7.64, 7.59 (2H, d); and δ 2.87 (6H, s). These values are consistent with literature values.[11b] (b) Pallenberg, A. J.; Koenig, K. S.; Barnhart, D. M. *Inorg. Chem.* **1995**, *34*, 2833−28440.

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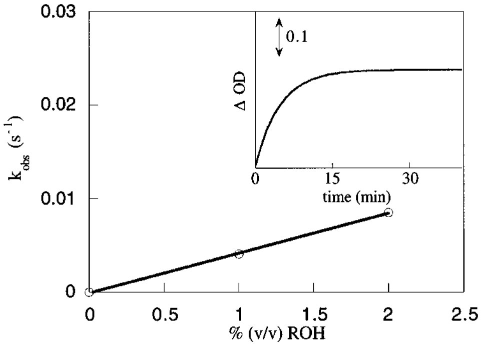
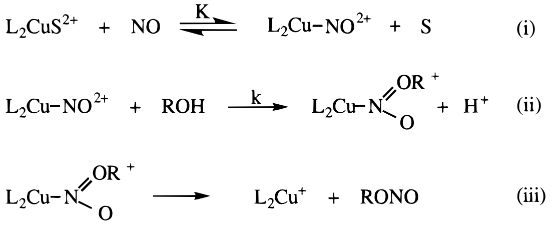


Figure 1. Dependence of k_{obs} for formation of $Cu(dmp)_2^+$ on methanol concentration in dichloromethane at 25 °C ($P_{NO} = 1$ atm). Inset: representative kinetic trace and its first-order fit.

Scheme 1. Proposed Mechanism for the Reduction of $Cu(dmp)_2^{2+}$ by NO in Hydroxylic Solvents



between the observed first-order rate constants (k_{obs}) for the formation of $Cu(dmp)_2^+$ and [MeOH] (Figure 1). However, at concentrations above ∼3%, the k_{obs} values increased in a nonlinear fashion, suggesting that the activity of the MeOH is affected by changes in the bulk solvent as methanol becomes a significant fraction.

The mechanism of this reaction is unlikely to follow an outer-sphere redox pathway since the calculated potential for simple electron transfer reaction between $Cu(dmp)_2^{2+}$ and NO is quite unfavorable ($\Delta E = -0.63$ V in aqueous solution). Thus, the sequence of reactions shown in Scheme 1 is proposed as a likely mechanism. This involves three key steps: (i) the reversible formation of an inner-sphere adduct between NO and Cu(II); (ii) reaction of this adduct with ROH to give an N-coordinated nitrite derivative; (iii) dissociation to the products, $Cu(dmp)_2^+$, RONO, and H^+.

In the solid state Cu(II) is frequently found to be five-coordinate;[13] indeed, there are two structures of salts of **I** which indicate the presence of a fifth ligand, nitrate in the case of the salt $[Cu(dmp)_2(NO_3)]NO_3$[13b] and H_2O in the case of $[Cu(dmp)_2(H_2O)](OTf)_2$.[13c] Therefore, an equilibrium between NO and solvent complexes as depicted in step i would be reasonable. In this context, Sykes and co-workers[14] suggested interconversion of a 5-coordinate Cu(II) to its 4-coordinate analog prior to electron transfer as being rate limiting in the $Fe(CN)_6^{4-}$ reduction of $Cu^{II}L_2^{2-}$ in aqueous solution (where L = 2,9-dimethyl-4,7-bis((sulfonyloxy)phenyl)-1,10-phenanthroline). Nonetheless, our attempts (by IR spectroscopy) to observe formation of a NO complex with **I** in the nonreactive solvent CH_2Cl_2 were not successful, probably because the equilibrium constant *K* is small at room temperature.

Step ii has some precedent in reactions of Ru(II)-coordinated NO with hydroxide to give the corresponding nitro complexes and of Ir(III) coordinated with alcohols to give isolable alkyl nitrite complexes.[15] The dependence of the overall rate on [MeOH] when the reaction was carried out in a mixed dichloromethane/methanol solution is consistent with step ii being rate-limiting. Since only a small change in the rate constant (k_{obs}) was observed when the reaction was carried out with added trifluoroacetic acid (CF_3CO_2H),[16] methanol rather than methoxide ion must be involved in this key step.

For comparison purposes, the reaction of $Cu(phen)_2^{2+}$ with NO was briefly examined. This proved to be very sluggish even in neat methanol ($k_{obs} < 10^{-6}$ s^{-1}), and only partial reduction was observed for a solution of $Cu(phen)_2^{2+}$ under NO atmosphere for several days. The behavior of $Cu(phen)_2^{2+}$ can be rationalized by its reduction potential, which is 0.5 V less positive than that of $Cu(dmp)_2^{2+}$. The potential difference is reflected in the ability of the methyl substituents in dmp to destabilize the Cu(II) state through steric interactions, while little repulsive steric interaction is expected for the tetrahedral Cu(I) state. Yandell et al. invoked the same argument to rationalize the substantially larger rate constant observed for the oxidation of ferrocytochrome *c* by $Cu(dmp)_2^{2+}$ (ca. 5 orders of magnitude) than that observed for the oxidation by $Cu(phen)_2^{2+}$.[17] The oxidizing power of $Cu(dmp)_2^{2+}$ was also reflected in its ability to be reduced by nitrite ion, NO_2^-, in methanol, while no reaction was observed for the analog $Cu(phen)_2^{2+}$.

The affinity of $Cu(dmp)_2^{2+}$ for NO suggested possibilities of applying it as a NO sensor in a solid state matrix. In this context, $[Cu(dmp)_2](OTf)_2$ was incorporated into a SiO_2 sol−gel matrix and the resulting solid material was exposed to NO.[18] The result was a rapid color change from yellow to green. This system could be "recycled" repeatedly (between NO and Ar or air) without any apparent decomposition. Unlike the reaction in solution, there were no permanent redox changes in the solid state reaction. The Cu oxidation state of the green product appears to be +2, as evident by the persistence of the ligand field absorption band (∼730 nm) in the visible region. Our preliminary EPR studies to probe the nature of the Cu(II)−NO interaction in the solid state have not been conclusive. Detailed studies of this solid state system and of the solution phase reductions of $Cu(dmp)_2^{2+}$ by NO and nitrite are in progress.

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